Ab Initio and Lattice Dynamics Computer Simulations of Inclusion Compounds(挿入化合物の第一原理計算と格子動力学コンピューターシミュレーション)

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論　文　内　容　要　旨

Chapter 1. Introduction

In order to better understand the nature of new phenomena and new properties of materials it is necessary to perform high level research. At the present time the numerical methods have begun to fill a highly important place in science. The emergence of powerful and high-speed computers provides a possibility to describe real systems and numerically solve the equations descriptive of behaviour systems at microscopic level.

The supramolecular chemistry is a highly interdisciplinary field that has rapidly expanded at the frontiers of chemical science with physical and biological phenomena. One of the main object of investigation in this field of science is inclusion compounds. The following structural features have been identified as attributes of a good host-guest system and represented desirable goals in the crystal engineering methodology of these compounds. There are: (a) the host molecules should form an invariant framework independent of the nature of the guest; (b) for a given host, it should be possible to accommodate a wide variety of guest species; and (c) the host properties should be capable of being tailored without changing the essential structure of the host. On the basis of these features, the structural, energetic, dynamical, and thermodynamical properties of many inclusion-type systems continue to present fundamental challenges to scientists.

The main aim of this thesis is a development of the lattice dynamics (LD) methods for molecular crystals. Also highly accurately first principles calculations are performed to determine structural and energetic properties of large size clusters. The main objects of our investigations are the inclusion compounds corresponding to class of molecular crystals. Despite of wide practical usage of these compounds in many fields of chemistry, physics and biology, the structural, energetic, dynamical, and thermodynamical properties of many inclusion-type systems still remain to be investigated.

Chapter 2. Theoretical Methods

The LD theory is very general and may be applied to a wide range of crystal types. However, it is not adapted to molecular crystals in the sense that the use of an atomic displacement coordinate basis not exploit the consequences of grouping atoms into molecules. Moreover, up to now, electrostatic interaction in the LD calculations of molecular crys-

tals has been taken into account, as a rule, by introducing into the potential energy terms describing the interaction of dipoles and higher multipoles localized at the molecules. However, if the distance between neighbouring molecules or some of atoms composing them is nearly equal to or smaller than the sizes of the molecules, it is necessary to take into account charges localized at the atoms. To make it properly one should use Ewald's formulae of summation, just as in the case of ionic and ionic-covalent crystals. The formulae describing the short-range and electrostatic parts of elements of the dynamicals matrix for any values of $\mathbf{q}$ wave vector is derived.

The well-known expressions for the calculation of the elastic moduli of ionic crystals are not suitable for molecular crystals since rotational degrees of freedom need not be considered. Here, analytical expressions appropriate for the elastic moduli of molecular solids are derived. The quasiharmonic approximation, used here, is adequate for the calculations of the thermal equation of state and the elastic moduli. The thermal magnitudes are determined here by the first and second derivatives of free energy $F_{qh} = U + F_s$ with respect to strain, where U is the potential energy of crystal and F_s is the vibrational part of the free energy. In LD approach the optimization scheme was developed for the ionic crystal in detail. For the molecular crystals, the optimization procedure is more complex with availability of rotation degree of freedom. The dynamical matrix of the crystal includes in this case translation, rotation and mixed terms. Another feature of our modeling is that the optimization is realized in combination with the dynamical matrix and elastic constant calculation and we have taken these values as a starting point for the optimization. This gives a possibility to study both the stability and structure variation of complex compounds with the minimum computer time.

The main formalisms of *ab initio* and density functional methods for ground state and configuration interaction method for excited state are also presented in this Chapter. Although many molecular chemical problems can be treated with Hartree-Fock method, the inclusion of correlation between the motions of the electrons within a molecular system is often required for quantitative predictions. Density functional theory (DFT) is a theory of electronic ground state structure, couched in terms of the electronic density distribution $n(r)$. It is an alternative, and complementary, approach to the traditional methods of quantum chemistry which are couched in terms of the many-electron wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. The computing time in DFT, for a many atom system with no geometrical symmetries, grows roughly like N_{at}^2 or N_{at}^3. This is much better than traditional methods, where computing time grows as $e^{\alpha N_{at}} (\alpha \approx 1)$. The DFT methods have applied to many different physical and chemical systems and will be useful to solve interesting problems in materials science. The Configuration Interaction (CIS) approximation seems to be reliable tools appropriate to study the properties of a wide-range of molecules in their excited states.

Chapter3. Cyclodextrin: New dimer configuration of guest in cyclodextrin

This chapter contains the experimental and computational studies on new dimer configuration of anthracene molecules in a γ-cyclodextrin. The different possible configurations of dimers both in free space and in *CyD* cavity are investigated by using *ab initio* and molecular dynamics (MD) calculations. We found that the anthracene dimer in the cavity is in a face-to-face (coplanar, S-shape) configuration (see Figure 1), which is quite different from the face-to-edge (T-shape) in gas phase. Their faces are slightly tilted and twisted. Excitation with the light (300–400 nm) forms intermolecular bonds between two anthracenes in a γ-cyclodextrin.

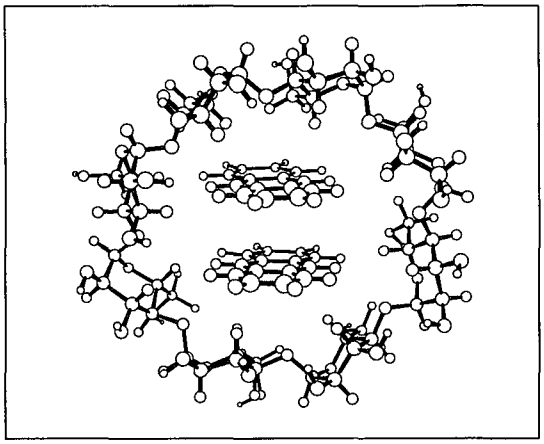

Figure 1. *Optimized anthracene dimer structure in CyD.*

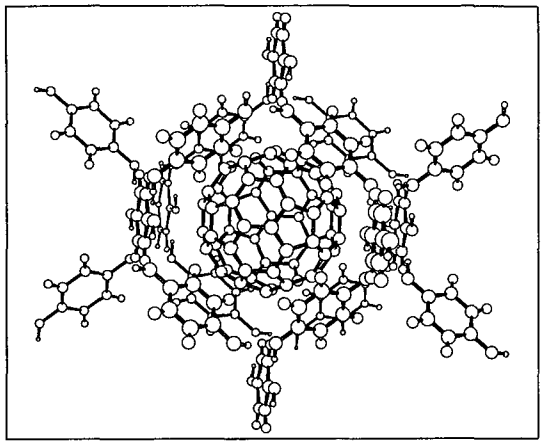

Figure 2. *Fragment of a crystal structure of HQ_3C_{60} complex.*

Absorption spectra were obtained from the reflection spectra of the powder sample using Kubelka-Munk formula. Differential spectra of samples before and after irradiation by the light (300–400 nm) show a broad absorption band. This band corresponds to the transition from the ground state to the excited state of the supramolecular complex. The *ab initio* calculations on excited states in anthracene reveal the most probable bonds between them, that which are the intermolecular bonds formed at the middle of them.

Chapter 4. Hydroquinone: Host configuration dependence on size of guest

A well-known so far β-form of hydroquinone (HQ_β) inclusion compounds have a double twofold interpenetration super-polonium host architecture with comparatively small cavities. These cavities are capable of accommodating different small guest molecules such as O_2, CO_2, HCN, CH_3OH, or CH_3CN. The dynamic properties of HQ_β clathrate with these guest molecules have been calculated by the LD method using AMBER force field. It has been shown that the contribution of the electrostatic interaction is at minimum for empty framework of HQ_β clathrate. However, Coulomb host-guest and guest-guest interactions are more essential in the cases of the encaged guests having large dipole moment like CO_2 and SO_2. The low frequencies of the host lattice are weakly dependent on the insertion of the guests into the cages. The most visible changes in dynamical properties of host lattice in high-frequency region are produced either by an asymmetrical guest like CH_3OH or a guest with a large dipole moment like CO_2 and SO_2.

The $(HQ)_3C_{60}$ complex (Figure 2) is the first example of a HQ_β inclusion compound with a single, extremely hollow super-polonium host network. The main features of this complex are that host structure of HQ_β is unstable when C_{60} molecules are not situated in the cages and that the molecular size and mass of C_{60} are far greater than that of the HQ molecule. The geometry of C_{60} in a cage has been calculated within the Hartree-Fock (HF) scheme. No charge transfer occurs in agreement with the previously experimental data. The stability and dynamical behaviour of this host structure are strongly dependent on the guest molecules and hence on guest-host interactions. This is a new aspect for inclusion chemistry, because previously the host-guest systems were described by investigation of two practically independent systems of host and guest structures.

Chapter 5. Urea: Structures and properties of small clusters

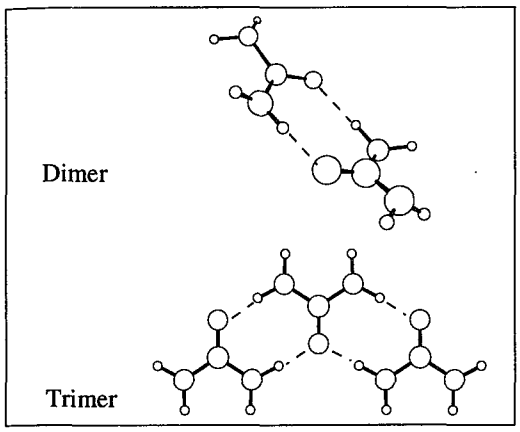

Figure 3. *Structure of most stable dimer and trimer of urea.*

In this section small clusters of urea have been investigated using much more accurate methods than have been applied previously. This is the first attempt to determine the equilibrium structure and frequencies of trimers by *ab initio* calculations. The cyclic structure of the dimer composed of two nonplanar molecules, just like the monomer, is most stable in the gas phase. A planar configuration for individual molecules, such as observed in crystal first occurs for trimer (see Figure 3). The interaction energy at the MP2 level is more accurate and inclusion of correlation effects is important for the description of H-bonding systems.

Nevertheless, for the cases considered here, BLYP calculations give a good description of energetic, dynamic, and electronic properties as compared with experimental data and can be used to investigate of hydrogen-bonded complexes where MP2 level is not available. The H-bonding interaction is important to stabilize planar geometry in small cluster, but is not sufficient to form this geometry in larger clusters or in crystal. The same type of H-bond is found in small clusters and in crystal. Stability of urea clusters is characterized by the maximum number of H-bonds (2 and 4 in dimer and trimer, respectively).

Chapter 6. Ices and Hydrates: Dynamical and thermodynamical stabilities

The dynamical and mechanical instabilities associated with the elastic moduli have been presented. The dynamical type is associated with the instability of acoustic modes of the phonon Hamiltonian at $\mathbf{q}$ =0 region. The mechanical instability is related to the fact that the equilibrium state of a crystal becomes thermodynamically unstable with respect to small homogeneous deformation of the crystal lattice when the stability conditions are violated for the isothermal or adiabatic moduli. In this case, the Gibbs free energy of the initial phase is always larger than that of the transformed phase at the point of the structural phase transition. The calculations on ice I_c, using the SPC potential for water interactions, show that one of the conditions for these moduli ($C_{11} - |C_{12}| > 0$) violated at $P \simeq$ 3-7 kbar and, as a consequence, the mechanical instability occurs. The dynamical instability occurs at much higher pressure. Stability of ice I_c is significantly increased with completely filled helium atoms. Moreover, the helium hydrate in ice I_c is more stable than ice $VIII$ in the pressure range of 4.24 to 5 kbar (see Figure 4). The detailed analysis of transition type along the pressure-induced melting-amorphization line of ice I_h (see Figure 5) shows that the transitions can be viewed as a crossover from a two-phase melting process towards a one-phase amorphization process (where the transition is induced by a mechanical instability limit of the solid). The calculated melting curve is in a good agreement with experimental points up to T=190K and extrapolates experimental points to the amorphization region. The calculated elastic instability curve is in reasonable agreement with experiment at $T <$ 150K but lies higher than the experimental points at more higher temperature.

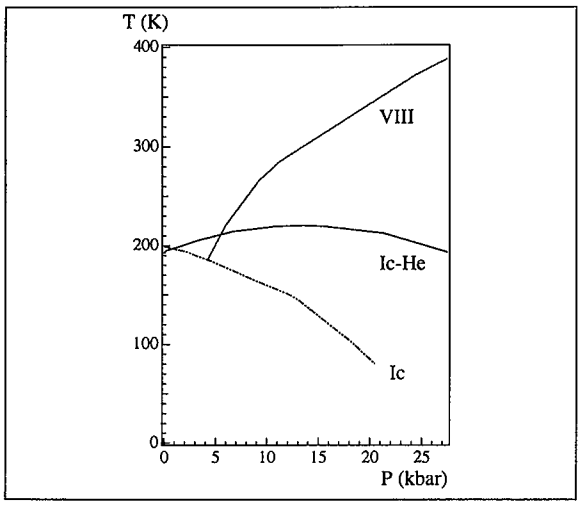

Figure 4. *Estimated curves of thermodynamical instability (melting curve) of ice I_c, $VIII$ and helium hydrate $He \bullet H_2O$ in ice I_c.*

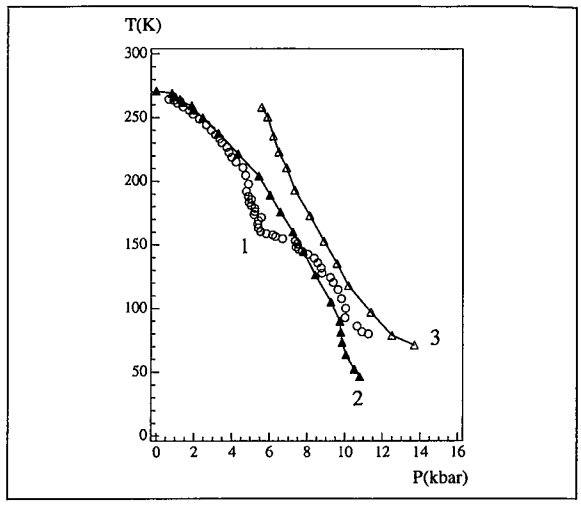

Figure 5. *The comparison of experimental melting-amorphization points (1) for I_h ice with theoretical melting (2) and mechanical instability (3) lines.*

The mechanical stability of the methane and xenon hydrates has been also investigated by LD approach. To solve the stability problem, elastic constant calculation, optimization of molecular positions, and cell shape at different P, T points have been performed in quasiharmonic approximation. The present numerical results give the mechanical instability pressure in the same region as it was observed experimentally for another hydrate. However, the different proton configurations have another structural behaviour and instability pressure. It can cause the indefiniteness in the experimental mechanical transition pressure after the glass transition at low temperature. To check these predictions, it is necessary hereafter to perform more detailed experimental investigations of hydrates in high pressure region.

Chapter 7. Conclusion

The conclusion of main results obtained by this thesis is given. The LD method for molecular crystals is introduced in this thesis. The formulation and general expressions for dynamic matrix have been presented taking into account both short-range and long-range (electrostatic) interactions. Moreover, general expressions for the elastic moduli of molecular crystal have been obtained within the framework of quasi-harmonic approximation, Also the optimization scheme in lattice approach is introduced. These expressions permit investigation of the dynamical properties in wide range of chemical compounds which form a class of molecular crystals and the stability of crystalline molecular system under variable pressures and temperatures through the monitoring of the Born stability conditions.

A variety of *ab initio* and *DFT* methods are also introduced and successfully applied for accurate calculations of physicochemical properties of some inclusion compounds. The feasibility of CIS theory for description of properties of molecules in excited states is checked and the reasonable agreement with experimental data is found. The results, presented in this thesis, provide a valuable information for experimental studies and can be used for future evolution of the theory of inclusion compounds.

審査結果の要旨

新物質・材料の創製において、原子レベルでの制御が可能となりつつある。その中で、各種原子や分子を内包した挿入化合物の持つ特異な構造と物性を基礎とした新材料は、その将来的発展が期待されるため、最近特に注目を集めている。本論文は、従来の理論の枠組みを越えた新たな定式化と超大規模シミュレーション計算により、各種挿入化合物の持つ特異な構造と物性の詳細を明らかにしたもので、全編７章よりなる。

第１章は序論である。

第２章では、本論文で用いる第一原理計算法と格子力学法の概要、本研究で新たに開発した分子性結晶に対する格子力学法、弾性定数の計算技法、分子性結晶の安定性解析法、及び分子性結晶の構造最適化法、基底状態に関する密度汎関数法、分子軌道法、励起状態を記述するための配置間相互作用法、について述べている。

第３章では、シクロデキストリン中のアントラセン２量体に関する第一原理分子軌道法計算を行った結果をまとめている。アントラセン２量体は、真空中では２つの分子が分子面を垂直にしたＴ型になっているが、シクロデキストリン中では、容積が小さいため平行に並んだＳ型になること、光照射で化学反応を起こして２つの分子面間が接合したり解離したりする可逆反応を起こすこと、等を励起状態を含めたシミュレーション計算によって示した。

第４章では、各種分子を内包したヒドロキノンの安定性を理論的に検討した結果を示した。C_{60}内包ヒドロキノンの電子状態を第一原理分子軌道法によって解析し、その安定構造を決定した。また、格子動力学法による振動状態計算により、系の光反応についての予測値を決定した。

第５章では、第一原理分子軌道法計算と局所密度近似を用いて、尿素分子の作るクラスターの構造最適化を行った。その結果、２量体は反った形での接合、３量体はほぼ平面での３角形を形成することが分かった。安定な結晶を実現するためには、挿入化合物を必要とすることも明らかにした。また、その振動解析を行い、エネルギー的に分離した伸縮モードと屈曲モードの２つの存在を確認した。

第６章では、氷の構造をSPCとTIP4Pポテンシャルを仮定して解析した。ヘルマン-ファインマン力を用いたダイナミカル行列を解くことによって格子振動を導出し、系の振動モードを議論した。また、自由エネルギーを計算して圧力・温度相図を求め、ヘリウムを内包した氷の新しい相の安定性を確認した。

第７章は結論である。

以上要するに、本論文は、第一原理計算法と格子力学法を用いて、挿入化合物の特異な構造と物性を明らかにしたもので、材料物性学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。